

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

New Alkylphenyl-Halo Triazines and process for their Manufacture

- We, CIBA LIMITED, a body organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 2-aryl-4:6-dichloro- and 2:4-diaryl-6-chloro-1:3:5-triazines are of considerable importance as intermediate products for the manufacture of vat dyestuffs. Hitherto, these compounds could only be made by a complicated method involving, for example, three stages by starting from dicyandiamide and the appropriate aryl-carboxylic acid chloride by way of the biuret and the aryl-guanamide (see British Specification No. 784,926).
- It is also known that cyanuric chloride can be reacted with a polycyclic aromatic hydrocarbon, for example, pyrene in the presence of aluminium chloride to form corresponding mono-chloro-triazine (see German Specification No. 877,938). When, however, benzene or naphthalene or a substitution product of either of these compounds is used in this reaction, a 2:4:6-triaryl-1:3:5-triazine is always obtained. (see U.S. Specification No. 1,734,029).
- The present invention provides the new compounds 2-(2':4'-dimethylphenyl)-4:6-dichloro-1:3:5-triazine and 2:4-di(2':4'-dimethylphenyl)-6-chloro-1:3:5-triazine, and a process for their manufacture.
- The present invention is based on the unexpected observation that the reaction of cyanuric chloride with meta-xylene, can be carried out in the presence of aluminium chloride in such a manner that 2-(2':4'-dimethylphenyl)-4:6-dichloro-1:3:5-triazine or 2:4-di(2':4'-dimethylphenyl)-6-chloro-1:3:5-triazine is obtained, as the main product. The reaction is advantageously carried out in the presence of an inert organic solvent, for example, an aromatic hydrocarbon such as benzene, or an aliphatic hydrocarbon having a boiling point below 150° C. It may also be carried out by using an excess of meta-xylene as solvent.
- For each molecular proportion of cyanuric chloride advantageously 1 to 5 molecular proportions of the meta-xylene and 1 to 2 molecular proportions of aluminium chloride are used.
- For the preparation of 2-(2':4'-dimethylphenyl)-4:6-dichloro-1:3:5-triazine preferably one molecular proportion of cyanuric chloride and about one molecular proportion of *m*-xylene are condensed in an inert organic solvent.
- For the preparation of 2:4-di(2':4'-dimethylphenyl)-6-chloro-1:3:5-triazine advantageously one molecular proportion of cyanuric chloride and two to six molecular proportions of meta-xylene are condensed in the presence of one to two molecular proportions of aluminium chloride and, if desired, in the presence of an inert organic solvent.
- The reaction is advantageously carried out at a temperature below 100° C., advantageously while stirring. As the reaction is exothermic, it is unnecessary to supply external heat.
- The reaction is advantageously worked up by introducing the reaction mixture into dilute hydrochloric acid, advantageously while cooling by the addition of ice. The solvent is advantageously removed by steam distillation. The crude product so obtained is advantageously purified by recrystallisation from an organic solvent and can be used in this form as a dyestuff intermediate. By reacting the product with an aminoanthraquinone, for example, valuable vat dyestuffs are obtained.
- The following examples illustrate the invention, the parts and percentages being by

weight unless otherwise stated, and the relationship of parts by weight to parts by volume being the same as that of the kilogram to the litre.

5

EXAMPLE 1

150 parts of ground aluminium chloride are introduced into a mixture of 500 parts by volume of meta-xylene and 184 parts of cyanuric chloride at 20—25° C., while stirring. The whole is stirred until the reaction product solidifies and then the whole is allowed to stand to give a total reaction period of 48 hours. The reaction mixture is then introduced into 2500 parts by volume of ice-water, to which 20 parts by volume of concentrated hydrochloric acid have been added, and the whole is thoroughly agitated. The xylene is distilled off in about 30 minutes by means of a strong current of

40

$C_{19}H_{18}N_3Cl$: Calculated: N=12.98%; Cl=10.95%
Found: N=13.15%; Cl=10.92%.

The compound so obtained can be converted, for example, by reaction with one molecular proportion of 1:4-diamino-2-(4'-chloro-benzoyl)-anthraquinone into a valuable blue vat dyestuff that yields dyeings fast to chlorine.

45

EXAMPLE 2

100 parts of ground aluminium chloride are introduced into a mixture of 175 parts of benzene, 53 parts of meta-xylene and 92 parts of cyanuric chloride at 20—25° C., while stirring, and the whole is stirred at the same temperature for 62 hours. The reaction mixture which is now a clear solution, is poured into 3000 parts by volume of cold water to which 50 parts by volume of concentrated hydrochloric acid have been added. After stirring the mixture for a short time, the benzene and xylene are distilled off in the course of 15 minutes by means of a strong current of steam. The solid residue is filtered while hot, pulverised, and dried at 100° C. *in vacuo*. There are obtained 100 parts of a crude product which are purified by dissolving it at the boil in 700 parts by volume of ligroin boiling at 120—135° C., with the addition of a small amount of animal charcoal. The solution is filtered and when cooled to 20° C. The product that crystallizes out is removed by filtration, washed with a small amount of petroleum ether boiling at 50—70° C. and dried. In this manner there are obtained 45 parts of pure 2-(2':4'-dimethylphenyl)-4:6-dichloro-1:3:5-triazine which crystallizes in prisms and melts at 135—136° C.

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Analysis: $C_{17}H_{14}N_3Cl_2$

Calculated: Cl=27.90%; N=16.54%

80

Found: Cl=27.80%; N=16.62%

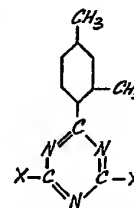
The product so obtained can be converted, for example, by reaction with 2 molecular proportions of 1:4-diamino-2-(4'-chloro-

benzoyl)-anthraquinone into a valuable blue vat dyestuff that yields dyeings fast to chlorine, or by reaction with two molecular proportions of 1-amino-4-methoxy-anthraquinone into a brilliant scarlet vat dyestuff.

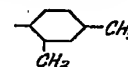
steam. The hot water is then decanted from the residue and the latter is dried *in vacuo* at 100° C. There are obtained 287 parts of a solid grey product which can be purified as follows:—
The whole of the product obtained is dissolved in 574 parts by volume of benzene. The solution is filtered and cooled to 35° C. 390 parts by volume of ethyl alcohol are added, while stirring, and then the whole is stirred for a further hour while cooling to 20° C. The product that crystallises out is filtered off, washed with a small amount of alcohol, and dried *in vacuo* at 90° C. There are obtained 180 parts of substantially pure 2:4-di-(2':4'-dimethyl-phenyl) - 6 - chloro-1:3:5-triazine melting at 132—133° C., and of which the melting point can only be slightly increased to 133.5—134.5° C. by further recrystallisation from benzene.

WHAT WE CLAIM IS:—
1. Triazine derivatives of the formula

90



in which one X represents a chlorine atom and the other X represents a chlorine atom or a residue of the formula



95

2. 2-(2':4'-dimethylphenyl)-4:6-dichloro-1:3:5-triazine.

3. 2:4-di-(2':4'-dimethylphenyl)-6-chloro-1:3:5-triazine.

4. A process for the manufacture of triazine derivatives, having the formula given in Claim 1, wherein cyanuric chloride is condensed with meta-xylene in the presence of aluminium chloride.

5. A process as claimed in Claim 4, wherein for each molecular proportion of cyanuric chloride 1 to 5 molecular proportions of the meta-xylene and 1 to 2 molecular proportions of aluminium chloride are used.

105

6. A process as claimed in Claim 4 or 5, wherein the reaction is carried out in the presence of an inert organic solvent.
- 5 7. A process as claimed in Claim 6, wherein benzene is used as the organic solvent.
8. A process as claimed in Claim 4 or 5, wherein one molecular proportion of cyanuric chloride and about one molecular proportion of meta-xylene in an inert solvent are condensed to yield 2-(2':4'-dimethyl-phenyl)-4:6-dichloro-1:3:5-triazine.
- 10 9. A process as claimed in Claim 8, wherein benzene is used as the organic solvent.
- 15 10. A process as claimed in Claim 4 or 4—6, wherein one molecular proportion of proportions of meta-xylene are condensed in the presence of one to two molecular proportions of aluminium chloride and, if desired, in the presence of an inert organic solvent to yield 2:4-di-(2':4'-dimethyl-phenyl)-6-chloro-1:3:5-triazine. 20
11. A process as claimed in any one of Claims 4—10, wherein the reaction is carried out at a temperature below 100° C. 25
12. A process for the manufacture of a triazine derivative conducted substantially as described in Example 1 or 2.
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